Ion Counter

This invention relates to method and apparatus for counting ions in a sample. More particularly, the invention relates to quantifying extremely low concentrations of ions in a gaseous medium.

In the book titled "Plasma chromatography" Edited by T.W. Carr and published in 1984 by Plenum Press (N-Y, London) there is described the measurement of concentrations of ions and molecules in a gas medium by means of electric current detection with an electrometer or other current detecting device. In a conventional electrical detector, based upon the Faraday cup, ions impinge on the collector and carry an electric charge. The voltage drop across the standard resistor connected to the collector is a measure of the ion current. The voltage signal from the resistor is then amplified by an amplifier. The measured and amplified ion currents are directly proportional to the number of ions and number of charges per ion. Therefore, the response of the Faraday cup depends upon the number of the ions collided with the collector. Faraday cup detectors are simple, inexpensive, rugged and reliable. They have high accuracy and constant sensitivity. The principal disadvantage of the Faraday cup is that the low detection limit of ions is relatively high. It is caused by its amplification system and electrical noise. Thus, this prior art method cannot be used to quantify extremely low concentrations of ions in gases.

It is known to use mass spectrometry to detect ions in a gas and to carry out a mass analysis of the ions and to identify the ions, e.g. a mass spectrometer is used as a detector coupled with gas chromatography. A mass spectrometer usually contains an electron multiplier connected to a measuring apparatus. In the electron multiplier electrons collide with surface elements and cause an electric current which is amplified in the measuring apparatus. Collision of charged particles with the surface is the main element of the ion detection. Thus, in both mass spectrometer and a

Faraday cup the ion detection is caused by transferring electric charges from ions to a surface connected to a measuring apparatus.

In a method for using a mass spectrometer for the identification of complex compounds, ions of the compound are generated by an ion source and these ions are then collided with neutral gaseous compounds to produce charged fragments of the ions, the mass spectra of these charged fragments are analysed and the identity of the original ions obtained from these spectra.

US Patents 4588889 and 5097124 disclose such methods.

In WO 99/30350 there is disclosed a method of analysing ions which is carried out in a mass spectrometer apparatus comprising an ion source, a linear RF quadrupole and a time of flight mass spectrometer. Ions are generated from the ion source and passed into the linear RF quadrupole. To retain ions within the linear RF quadrupole, potentials are applied to either end of it and it is then operated as an ion trap. Ions of interest are selected in the linear RF quadrupole and unwanted ions are caused to be ejected. Selected ions are then excited and caused to collide with a neutral gas, to cause collision induced dissociation thereof, thereby forming fragment ions for analysis in the time of flight mass spectrometer. The potential of one end of the linear RF quadrupole is then adjusted to pass selected and fragment ions through to the time of flight mass spectrometer. This enables a spectrum of the selected and the fragment ions to be obtained from the time of flight mass spectrometer.

In these methods of using a mass spectrometer, a charged ion is produced and this charged ion is split into charged fragments which are subjected to an electric field and a mass spectrometric analysis to obtain a spectrum and to identify the compound.

However this is not the same as counting the number of ions in a gaseous sample and such methods cannot be used to count the number of ions.

An important practical disadvantage of using a mass spectrometer is that it requires a vacuum for the separation and detection of ions and it cannot operate under the atmospheric pressure. Thus, mass spectrometry cannot be employed to quantify *in-situ* extremely low concentrations of ions in gases because mass spectrometry requires the use of a vacuum and complex and expensive equipment.

In addition, the lowest limit for the concentration of ions which can be detected and quantified with a mass spectrometer is relatively high; this is because of the electrical noise within amplification system and losses caused by the interface to the vacuum system.

We have devised a method and apparatus for counting the number of ions in a gaseous sample which overcomes these problems.

Accordingly, one aspect of the present invention provides a method of counting the number of ions in a gaseous sample which method comprises (i) colliding the ions with uncharged particles of greater mass than the ions to transfer charge from said ions to the uncharged particles to produce charged particles (ii) subjecting the charged and uncharged particles to an electric field to separate the charged particles from the uncharged particles and (iii) numerically counting the number of charged particles.

The electric field preferably directs the charge particles to a counting means which can count the number of particles.

According to another aspect of the invention there is provided an apparatus for counting the number of ions in a gaseous sample which apparatus comprises (i) a mixing chamber (ii) a first inlet in the mixing chamber through which a gaseous sample containing ions can enter (iii) a second inlet in the mixing chamber through which uncharged particles entrained in a gas can enter so that the ions and uncharged

particles collide (iv) an outlet from the mixing chamber which discharges to a separation chamber which separation chamber has an electric field generating means and an outlet discharging to a charged particle detecting and numerically measuring means.

The electric field generating means is arranged to be able to subject particles in the separation chamber to an electric field.

The ions and uncharged particles collide with each other as a result of Brownian diffusion and some of the uncharged particles become charged by transfer of charge from the ions.

The charge transfer can occur when a neutral particle and an ion collide to produce a charged particle with a molecule/atom on its surface formed when the ion transfers its charge to the particle. Thus, after the transfer event the particle acquires the charge and keeps the neutralised ion.

Another way the charge transfer a neutral particle can occur is when the particle and an ion collide to produce a particle with an ion on its surface. Thus, after the transfer event the particle acquires the ion and becomes charged.

A third way of the charge transfer a neutral particle can occur is when a particle and an ion collide to produce a charged particle. The ion becomes a neutral molecule/atom and leaves the surface of the particle. Thus, after the transfer event, the particle acquires the charge. The neutralised ion moves in the gas phase separately.

It is not important if both particle and ion are involved in chemical reactions with each other or with third parties. The important point is the charge has to be transferred from an ion to a particle.

In the separation chamber the charged and uncharged particles are separated according to their electric mobility by the imposition of the electric field so that the gas flow from the outlet of the separation chamber contains only charged particles.

In order that all the ions collide with an uncharged particle the number concentration of uncharged particles is in excess of the number concentration of the ions and, more preferably, greatly in excess.

The ions and the uncharged particles are preferably entrained in a gaseous flow and enter the mixing chamber where they collide; preferably they are entrained in air. The uncharged particles and the ions may or may not react when they collide providing a charge transfer event occurs.

The uncharged particles are preferably formed as an aerosol e.g. by using an evaporator and condensation means to produce the uncharged aerosol particles.

The charged particles can be detected and counted individually by means of single particle counting means. The means for counting the particles can be a commercially available optical particle counter such as MetOne (Pacific Scientific Instruments). This optical particle counter enables aerosol particles of the diameter greater than 0.3 μm to be individually counted. Other particle counting means may also be utilised such as light scattering or light absorption detectors or a dust monitor, nephelometer, aethelometer or a condensation particle counter.

The electric field generating means can be two spaced apart electrodes with an electric field generated between them, preferably the electric field is at least 2,000/volts per cm. Typically filed strengths of 5,000 volts/cm to 20,000 volts/cm can be used. Preferably a gaseous flow containing charged and uncharged particles is passed between the electrodes, typically the electrodes can be of the order of 5mm apart.

Since the charged particles have acquired the electric charges following collisions with ions, the number of charged particles is substantially directly related to the number of ions in the mixing chamber. For unit flow rates, the number of ions in the mixing chamber is proportionate to the number of ions which entered the mixing chamber in the gaseous flow so that the concentration of charged particles is a measure of the concentration of ions in the gaseous sample.

If necessary a correction factor which links the actual concentration of ions with the number concentration of charged particles can be found by means of calibration using mass spectrometry or another suitable techniques.

The flow rates of the gases in the separation chamber have to satisfy "the laminar flow criterion": the linear velocity of the flows have to be equal to prevent turbulence.

Any type of semi-volatile material can be used to generate aerosol particles, for instance glycerol or sulphur. These aerosol particle, suspended in a gas, may be either liquid or solid. Aerosol particles may be produced from a mixture of organic compounds or inorganic substances. Atmospheric aerosol particles may also be used to accept charges in the mixing chamber. Aerosol particles may be also generated from a dust or from a liquid using an atomiser as well as a nebuliser. Particles may also may be in a liquid in the form of a hydrosol or emulsion. Particles generated in these ways have charges. These charges have to be removed by means of a charge neutralisation or removal means employed to remove charged particles from the aerosol flow.

An ion mobility selection unit may be attached to the inlet of the mixing chamber to enable ions of pre-determined mobility to pass into the mixing chamber. Thus, the ions with such pre-determined mobility are selected for the detection and measurement.

An ionisation chamber containing means for effecting ionisation of molecules or clusters of interest to produce ions from non-ionic molecules or clusters may be attached to the inlet of the mixing chamber. This enables a wide range of species, e.g. molecules, free radicals, clusters, nano-particles, and atoms, to be detected and quantified. The ionisation means may comprise a method of ionisation with a degree of selectivity for instance UV radiation of about 10 or 11 eV, in the case of photo-ionisation, the ionisation selectivity may be achieved by choosing the gas containing molecules or atoms with a higher ionisation potential than the energy of the UV source.

For detection of trace species in liquids or solids a liquid or a solid sample may be evaporated first into a gas medium and then treated as a gas sample. Alternatively, a liquid or solid sample may be heated to a predetermined temperature first to release some of the trace species in a gas medium and then the gas medium containing the trace species may be treated as a gas sample.

A plurality of mixing chambers, arranged in series or in parallel, can be used and a plurality of selection chambers, or particle generator means, arranged in series or in parallel can also be used.

Where advantageous, other detectable species such as clusters, nano-particles, and molecules suspended in a gas may be used instead of uncharged aerosol particles.

If desired, a condensation unit, adapted to increase the size and the mass of the charged aerosol particles or the detectable species may be positioned between the separation chamber and the charged particle detecting and numerically measuring means.

Optionally charge neutralisation or charge removal means may be positioned in flows at the second inlet containing uncharged particles to ensure the neutrality of such flows.

If desired, a differential mobility analyser may serve as separation chamber providing a single output or plurality of outputs according to particle mobility.

Counting particles enables very low concentrations of ionised matter to be quantified on-line, e.g. concentrations as low as $1/cm^{-3}$ may be measured reliably. Conventional equipment to count ions in a gas is reliable only down to concentrations of 10^5 $/cm^{-3}$, thus the present invention is a great improvement over currently used methods and apparatus.

The invention will now be described, by way of example, with reference to the accompanying schematic drawings in which:

FIGURE 1 shows schematically an apparatus for detecting the presence of, and measuring extremely low concentrations of ions in gases;
FIGURE 2 is a schematic view of the separation chamber together with some associated equipment and
FIGURE 3 shows schematically examples of charge transfer

Referring to fig. 1, there is shown a mixing chamber (2) having a first inlet (1) for a sample gas flow containing ions, a second inlet (3) for uncharged aerosol particles entrained in a flow of air and an outlet (4) discharging to a separation chamber (5). The outlet from the separation chamber (5) discharges through connector (6) to optical particle counter (7). There is an exhaust outlet (13) from counter (7).

Referring to fig. 2 the separation chamber (5) is provided with electrodes (11), producing an electric field, there is an outlet (12), a pump means (9) and an aerosol

fibre filter means (10) connected to a third inlet (8) to chamber (5). The electrodes (11) are positioned at upper and lower regions of the chamber (5), the inlet (8) and the outlet (6) are respectively positions at the upper region of the chamber, whilst the inlet (4) and outlet (12) are respectively positioned at the lower region. Flow dividing baffles (14) are positioned in end regions of the chamber.

Referring to fig. 1 in operation, sample gas containing ions enters the mixing chamber (2) through the first inlet (1) with the flow of the gas sample effected either by force flow maintaining means (not shown) at the inlet or induced flow maintaining means (not shown) at the exhaust outlet (13) from the apparatus. In the mixing chamber (2), the sample gas flow containing the ions is mixed with the air flow carrying the uncharged aerosol particles introduced into the mixing chamber (2) through the inlet (3) with the concentration of the uncharged aerosol particles greatly in excess of the concentration of ions. The ions and aerosol particles collide with each other as a result of Brownian diffusion and some of the aerosol particles become charged by transfer of charge from the ions. Thus, the flow discharged from the mixing chamber (2) contains both charged and uncharged aerosol particles and passes to the separation chamber (5), where charged and uncharged aerosol particles are separated according to their electric mobility by the imposition of the electric field to the effect that at the outlet (6) from the chamber (5) the gas flow contains only charged aerosol particles.

The charged aerosol particles entrained in the gas flow discharge through connector (6) into the optical particle counter (7) where the charged aerosol particles are detected and counted. Since the charged aerosol particles have acquired the electric charges following collisions with ions, the number of charged aerosol particles is substantially related to the number of ions in the mixing chamber (2). For unit flow rates, the number of ions in the mixing chamber (2) is proportionate to the number of ions entered the mixing chamber (2) in the sample gas so that the concentration of charged particles is indicative of the concentration of ions in the sample gas.

A correction factor that links the actual concentration of ions with the number concentration of charged particles can be found by means of calibration using mass spectrometry or another suitable techniques.

Referring to fig. 2 (which may be in the form of a commercially available differential mobility analyser column) following separation, the gases with entrained neutral particles are recycled through an outlet (12), a pump means (9) and an aerosol fibre filter means (10) to an inlet (8). In operation, the gas flow with both charged and neutral aerosol particles enters the separation chamber (5) through the inlet (4) and the neutral particles are carried with the gas flow to the outlet (12). The charged particles are urged upwardly and towards the outlet (6) by the effect of the electric field generated by the energised electrodes (11). The uncharged particles leave the separation chamber (5) at outlet (12) and are pumped by pump (9) through filter (10) to inlet (8) of chamber (5). The baffles (14b) facilitate the separation of the charged and uncharged particles. The charged particles entering chamber (5) through inlet (4) are thereby urged into the flow of filtered gas from the inlet (8). The flow rates of the gases in the separation chamber (5) have to satisfy "the laminar flow criterion": the linear velocity of the flows have to be equal.

In an embodiment of the apparatus used in the example below, the mixing chamber (2) was manufactured from brass having the shape of a cylinder of the internal volume of 0.5 litres. All the inlets and connectors were made from brass and copper. The separation chamber (5) was of rectangular cross-section and manufactured from aluminium with copper electrodes (11) insulated and placed inside the chamber. The distance between the electrodes was 5 mm and the voltage was from 1000 to 10,000 Volts DC.

Referring to figure 3 one way of the charge transfer is shown in figure 3a. A neutral particle (21) and an ion (22) collide to produce a charged particle (23) with a molecule/atom on its surface formed when the ion transfers its charge to the particle.

Thus, after the transfer event the particle acquires the charge and keeps the neutralised ion.

Another way of the charge transfer is presented in Figure 3b. A neutral particle (24) and an ion (25) collide to produce a particle (26) with an ion on its surface. Thus, after the transfer event the particle acquires the ion and becomes charged.

A third way of the charge transfer is shown in Figure 3c. A neutral particle (27) and an ion (28) collide to produce a charged particle (29). The ion becomes a molecule/atom (30) and leaves the surface of the particle. Thus, after the transfer event, the particle acquires the charge. The neutralised ion moves in the gas phase separately.

Example

In the Example a commercial optical aerosol particle counter MetOne (Pacific Scientific Instruments) was used to count particles. This optical particle counter enables aerosol particles of the diameter greater than 0.3 μm to be individually counted.

In a test, ions have been formed in the air using ^{241}Am (0.9 μCi) α -particle emitter. Uncharged aerosol particles were generated from glycerol by an aerosol generator based upon gas-to-particle conversion mechanism. The particle number concentration depends upon the flow rate through the aerosol generator and evaporation temperature. The number concentration of glycerol particles was in the range from 10^9 to 10^{12}/m^{-3}. The flow rate was maintained by a pump and quantified by a rotameter: the range of the flow rate was from 0.2 to 2 litres/min.

The apparatus of figs. 1 and 2 was used to count the number of ions, and the sample air flow containing the ions was drawn to the mixing chamber (2) through the inlet

(1) by an exhaust pump (not shown) connected to the optical particle counter (7) to mix with the uncharged glycerol aerosol particle flow in the mixing chamber. In the mixing chamber (2) the ions collided with the uncharged glycerol aerosol particles and some of aerosol particles became charged. The flow discharged from the mixing chamber (2) contained both charged and uncharged glycerol aerosol particles and the flow containing the charged and uncharged aerosol particles than entered the separation chamber (5), through the outlet connector (4). In the separation chamber (5), charged and uncharged glycerol aerosol particles were separated according to their electric mobility in the electric field such that at the outlet (6) of the chamber (5) the gas flow contained only charged glycerol aerosol particles of about 1 μm mean diameter. The charged glycerol aerosol particles were carried by the gas flow through the outlet connector (6) into the optical particle counter (7). The concentration of ions in the air formed by the radioactive source ^{241}Am was found to be 2×10^2 cm^{-3}. In other experiments, recorded concentrations were in the range from 7 to 3000 cm^{-3}.

It will be appreciated that an ion mobility selection unit may be attached to the inlet (1) to enable ions of pre-determined mobility to pass into the mixing chamber (2). Thus, the ions with such pre-determined mobility are selected for the detection and measurement.

It will further be appreciated that an ionisation chamber containing means for effecting ionisation of molecules or clusters of interest, for instance UV radiation of about 10 or 11 eV may be attached to the inlet (1) of the mixing chamber. This enables a wide range of species, e.g. molecules, free radicals, clusters, nano-particles, and atoms, to be detected and quantified.

If desired, a condensation unit, adapted to increase the size and the mass of the charged aerosol particles or the detectable species may be positioned between the separation chamber (5) and the charged aerosol particle detector (7)

Where appropriate, charge neutralisation or charge removal means may be positioned in flows at the inlet (3) and (8) containing uncharged aerosol particles to ensure the neutrality of such flows.

If desired, a differential mobility analyser may serve as separation chamber (5) providing a plurality of outputs according to particle mobility.